THE Cs-U-O PHASE DIAGRAM
AND ITS APPLICATION TO
URANIUM-PLUTONIUM OXIDE FAST REACTOR FUEL PINS

by

D. C. Fee, I. Johnson, S. A. Davis, W. A. Shinn,
G. Staahl, and C. E. Johnson

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ABSTRACT

Portions of the cesium-uranium-oxygen system have been
investigated between 873 and 1273 K and a phase diagram has been
constructed using our data and the data of other workers in the
field. Thermodynamic and kinetic data have been used to examine
the reactions that occur in fast-reactor fuel pins between fission-
product cesium and the uranium oxide blanket. It was concluded
that at the low oxygen potentials existing at the interface between
the uranium-plutonium mixed-oxide and the uranium oxide blanket,
Cs_2UO_4 is the only Cs-U-O compound expected to be formed in the
uranium oxide blanket.

I. INTRODUCTION

In uranium-plutonium mixed-oxide fast-reactor fuel pins, fission-product
cesium has been observed to migrate axially, and high localized concentrations
have been observed at the interface of the mixed-oxide fuel and the uranium
oxide axial blanket.[1-13] These high concentrations of cesium have been
associated with a "two-phase" region, which presumably is uranium oxide and a
(mixture of) ternary Cs-U-O compound(s).[4,5,8,10,13] Moreover, cladding deforma-
tion[1,12,13] and cladding breach[7,8,10] adjacent to the fuel-blanket interface
have been observed; these conditions of deformation and breaching could be
explained by the formation of a low-density Cs-U-O compound. Gas-flow restric-
tions in prototypical gas-cooled fast-reactor fuel pins,[14] which can deleteriously
affect the pressure equalization system of the fuel pin,[15,16] have also been
attributed to the formation of a Cs-U-O compound. With the formation of a low-
density Cs-U-O compound, an increase in volume occurs, the extent of which will
depend on the composition of the compound because there are large differences
in the molar volumes of Cs-U-O compounds: 86, 130, and 213 cm^3 for Cs_2UO_4,[17]
$Cs_2U_2O_7$,[17] and $Cs_2U_4O_{12}$,[18] respectively. (In comparison, the molar volume of
UO_2 is 24.6 cm^3.[19]) The Cs-U-O compound or compounds present at the interface
between fuel and blanket have not been determined in irradiated mixed-oxide fuel
pins, and a literature survey of phase equilibria in the Cs-U-O system yielded
incomplete and even conflicting data as to the cesium uranate(s) that might be
expected to form. Therefore, phase studies of the Cs-U-O system were undertaken
in the areas in which published data are in conflict in an effort to establish
a consistent phase diagram for the Cs-U-O system and to define the composition
of the cesium uranate(s) formed at the fuel-blanket interface in irradiated
mixed-oxide fuel. Thermodynamic and analytical data derived at ANL, as well
as literature data, were used in the construction of the diagram.

In uranium oxide-blanketed mixed-oxide fuel, two factors important to the formation of cesium uranate(s) at the fuel-blanket interface are temperature and oxygen potential ($\Delta \bar{G}_{O_2}$ = RT ln P_{O_2}). These factors are sufficiently well known to allow the results of out-of-pile experiments to be related with some degree of confidence to in-pile fuel behavior. Studies at ANL have indicated that the oxygen potential depends on the deviation from stoichiometry of uranium oxide (x in UO_{2+x}),[20,21] as well as on temperature, which, near the fuel-blanket interface, ranges upward from 873 K. The stoichiometry of the blanket pellets may vary from stoichiometric uranium dioxide to $UO_{2.01}$ or higher, depending on the extent of oxidation of the initially stoichiometric pellets during storage prior to loading the fuel pin. Stoichiometric uranium dioxide has an O/U atom ratio of exactly two and an oxygen potential of -640 kJ/mol at 873 K and -573 kJ/mol at 1273 K. The oxygen potential of $UO_{2.01}$ is -256 kJ/mol at 873 K and -248 kJ/mol at 1273 K. The cesium pressure (or activity) at the fuel-blanket interface has not been experimentally determined. Consequently, out-of-pile experiments relevant to the formation of a Cs-U-O phase in the uranium oxide blanket of irradiated uranium-plutonium mixed-oxide fuel pins must include temperatures of 873 K and higher, oxygen potentials more negative than -210 kJ/mol, and cesium pressures (activities) up to and including that of liquid cesium.

Table 1 is a condensation of information on the Cs-U-O system found in the literature. The following are highlights from the table. (1) Efremova *et al.*,[22] Cordfunke *et al.*,[17] and van Egmond[18,29-31] heated mixtures of Cs_2CO_3 and UO_3 in air and obtained compounds whose compositions varied from Cs_2UO_4 to $Cs_2U_{15}O_{46}$. However, none of the Cs-U-O compounds formed had a uranium valence of five, and only three compounds, $Cs_2U_4O_{12}$, $Cs_2U_6O_{18}$ and $Cs_2U_9O_{27}$, had a net uranium valence of less than 6. (2) The compounds obtained by these three groups of researchers[17,18,22,29-31] and by Spitzyn *et al.*[26,27] were found to decompose to $Cs_2U_4O_{12}$ when heated in air at temperatures above 1173 K. (3) At oxygen pressures less than 10^{-5} Pa, Cordfunke reported that only the $Cs_2U_4O_{12}$-UO_2 phase region was stable above 873 K (and concluded that $Cs_2U_4O_{12}$ was the compound of interest in mixed-oxide fuel rods). (4) Venker,[34] Aitken,[37] Adamson,[37,38] and Aubert[36] found that the hexavalent cesium uranates, Cs_2UO_4 or $Cs_2U_2O_7$, were stable at temperatures above 873 K in equilibrium with gaseous cesium and urania, in contrast to Cordfunke's findings. (5) Aitken[37,39] and Adamson[41] reported that pentavalent uranates, $Cs_{1.3}UO_3$ or $Cs_{0.5+x}UO_3$ (x = 0-0.5), exist in equilibrium with liquid cesium and $UO_{2.00}$. This is in conflict with the findings of Efremova,[22] Cordfunke *et al.*,[17] van Egmond[18,29-31] and Rudorff *et al.*[24,25] who found no pentavalent cesium uranate, $CsUO_3$, even though such compounds as $NaUO_3$,[23] KUO_3[32] and $RbUO_3$[32] have been reported.

Efremova *et al.*[22] reported that after heat treatment at 873 K in air of various mixtures of Cs_2CO_3 and UO_3, the ternary compounds Cs_2UO_4, $Cs_2U_2O_7$, $Cs_2U_3O_{10}$, $Cs_2U_4O_{13}$, and $Cs_2U_6O_{19}$ were identified by X-ray diffraction analysis. A cesium analog of ternary uranium(V) oxides such as $NaUO_3$[23] or Na_3UO_4[23] was not reported.[22] After heating various mixtures of Cs_2CO_3 and UO_3 in air at 873 K, Cordfunke *et al.*[17] and van Egmond[18,29-31] identified distinct X-ray patterns for Cs_2UO_4, α- and β-$Cs_2U_2O_7$, $Cs_4U_5O_{17}$, α-, β- and γ-$Cs_2U_4O_{12}$, $Cs_2U_4O_{13}$, $Cs_2U_5O_{16}$, $Cs_2U_6O_{18}$, $Cs_2U_7O_{22}$, $Cs_2U_9O_{27}$, and $Cs_2U_{15}O_{46}$. Of these, $Cs_2U_4O_{12}$, $Cs_2U_6O_{18}$, and $Cs_2U_9O_{27}$ have a net uranium valence less than 6+. The compound $CsUO_3$ was not observed; under similar conditions, KUO_3 and $RbUO_3$ were observed.[32] Cordfunke *et al.*[17] presented their observation in the form of a psuedo-binary phase diagram at P_{O_2} = 2 x 10^4 Pa over the temperature range 300-1500 K.

Table 1. Literature Information on the Cesium-Uranium-Oxygen System

Reactant(s)	Products	Experimental Conditions	Reference
$Cs_2CO_3 + UO_3$	Cs_2UO_4, $Cs_2U_2O_7$, $Cs_2U_3O_{10}$, $Cs_2U_4O_{13}$, $Cs_2U_6O_{19}$	heated in air at 873 K	Efremova *et al.* (Ref. 22)
$Cs_2CO_3 + UO_3$	Cs_2UO_4, $Cs_2U_2O_7$ (α and β), $Cs_4U_5O_{17}$, $Cs_2U_4O_{12}$ (α, β, and γ), $Cs_2U_4O_{13}$, $Cs_2U_5O_{16}$, $Cs_2U_6O_{18}$, $Cs_2U_7O_{22}$, $Cs_2U_9O_{27}$, $Cs_2U_{15}O_{46}$	heated in air at 873 K	Cordfunke *et al.* (Ref. 17) and van Egmond (Refs. 18, 29-31)
Cs_2UO_4, $Cs_2U_2O_7$ $Cs_4U_5O_{17}$, $Cs_2U_4O_{12}$ $Cs_2U_4O_{13}$, $Cs_2U_5O_{16}$ $Cs_2U_6O_{18}$, $Cs_2U_7O_{22}$ $Cs_2U_9O_{27}$, $Cs_2U_{15}O_{46}$	$Cs_2U_4O_{12}(+U_3O_8)$	heated in air, T > 1323 K	Cordfunke *et al.* (Ref. 17)
Cs_2UO_4	$Cs_2U_4O_{12}$	heated in air, T > 1273 K	Spitzyn *et al.* (Refs. 26, 27)
$Cs_2U_2O_7$	$Cs_2U_4O_{12}$	heated in air for 6 hr at 1473 K	Spitzyn *et al.* (Ref. 27)
$Cs_2U_3O_{10}$, $Cs_2U_4O_{12}$, $Cs_2U_6O_{19}$	$Cs_2U_4O_{12}$	heated in air for 6 hr at 1273 K	Spitzyn *et al.* (Ref. 27)
Cs_2UO_4, $Cs_2U_2O_7$ $Cs_4U_5O_{17}$, $Cs_2U_4O_{12}$ $Cs_2U_4O_{13}$, $Cs_2U_5O_{16}$ $Cs_2U_6O_{18}$, $Cs_2U_7O_{22}$ $Cs_2U_9O_{27}$, $Cs_2U_{15}O_{46}$	$Cs_2U_4O_{12}(+UO_2)$	$P_{O_2} < 10^{-5}$ Pa T > 873 K	Cordfunke[33]
$Cs(g)^a + UO_{2.1}$	Cs_2UO_4 or $Cs_2U_2O_7$	heated for 340 hr at 973 K in stainless steel capsule	Venker *et al.* (Ref. 34)

(contd)

Table 1. (contd)

Reactant(s)	Products	Experimental Conditions	Reference
$Cs(g) + UO_{2.00} (^{+.01}_{-.00})$	Cs_2UO_4 + stoichiometric urania	1023 K (in Mo capsule for 100 hr in a thermal gradient)	Aitken *et al.* (Ref. 37)
$Cs(g)^b + UO_3$	Cs_2UO_4 + stoichiometric urania	heated in Mo capsule for 100 hr at 1123 K	Adamson *et al.* (Ref. 37,38)
$Cs_2O + UO_2$	$Cs_2U_2O_7$ (2 experiments)	heated in stainless steel capsule for: a) 1500 hr at 1073 K b) 1000 hr at 1273 K	Aubert *et al.* (Ref. 36)
$Cs_2O + UO_{2.05}$	$Cs_2U_2O_7$ (4 experiments)	heated in stainless steel capsule for: a) 2000 hr at 973 K b) 1500 hr at 1073 K c) 1000 hr at 1173 K d) 1000 hr at 1273 K	Aubert *et al.* (Ref. 36)
$U_3O_8 + Cs_2O_x + Cs(\ell)$ (x = 2.5 ± 0.5)	$Cs_{1.3}UO_3$ [in equilibrium with $UO_{2.00} + Cs(\ell)$]	heated in Ni capsule for 100 hr at 1073 K	Aitken *et al.* (Refs. 37, 39)
$Cs(\ell) + Cs_2UO_4$	$Cs_{1.3}UO_3 + Cs(\ell)$	heated in Ni capsule for 113 hr at 1000 K	Aitken *et al.* (Ref. 37, 39)
$Cs(\ell) + Cs_2UO_4 + UO_{2.00}$	$Cs_{0.5} + xUO_3 + Cs(\ell) + UO_{2.00}$ (x = 0 - 0.5)	emf cell at 873 K	Adamson *et al.* (Ref. 41)

[a]Cesium pressure = 1.35×10^5 Pa.

[b]Cesium pressure = 2.5×10^3 Pa.

At temperatures above 1323 K, Cordfunke et al.[17] reported that $Cs_2U_4O_{12}$ is the only stable cesium uranate formed in air. Rudorff et al.[24,25] confirmed that $CsUO_3$ does not form in the Cs-U-O system when Cs_2UO_4 and UO_2 are heated at temperatures above 873 K in a sealed quartz tube. Under similar conditions, ternary uranium oxides with the composition MUO_3 (where M = Li, Na, K, and Rb) were formed from the reaction of M_2UO_4 with UO_2.[24,25]

Spitzyn et al.[26,27] reported that Cs_2UO_4 was stable when heated in air for up to 6 hr at 1173 K, but that it decomposed into a different Cs-U-O phase when heated in air at 1273 K or higher temperatures for 6 hr.[26] The same Cs-U-O decomposition product[27] was observed by X-ray diffraction when several other cesium uranates were heated in air for 6 hr at different temperatures: $Cs_2U_2O_7$ heated at 1473 K; $Cs_2U_3O_{10}$, at 1273 K; $Cs_2U_4O_{13}$, at 1273 K; and $Cs_2U_6O_{19}$, at 1273 K. Efremova et al.[28] and Cordfunke et al.[17] identified this decomposition product as being $Cs_2U_4O_{12}$ (with a net uranium valence of less than 6+); however, the two groups reported different X-ray patterns for the compound.

Cordfunke[33] reported that at oxygen pressures less than 10^{-5} Pa, only the $Cs_2U_4O_{12}$-UO_2 phase region was stable above 873 K. All cesium uranates reported by Cordfunke et al.[17] and van Egmond[18,29-31] decomposed to $Cs_2U_4O_{12}$ + UO_2 after one week at temperatures above 873 K. Cordfunke concluded that $Cs_2U_4O_{12}$ was the compound of interest in mixed-oxide fuel rods.

Hexavalent cesium uranates have been reported at temperatures above 873 K and low oxygen potentials. In a 340-hr simulation study at 973 K and using a stainless steel capsule, Venker et al.[34] identified Cs_2UO_4 or $Cs_2U_2O_7$ by X-ray diffraction analysis as the product of the reaction of gaseous cesium $(1.3 \times 10^5$ Pa) with $UO_{2.1}$. The oxygen potential[20] of $UO_{2.1}$ at 973 K is -215 kJ/mol. The oxygen potential in the stainless steel capsule was probably somewhat more negative due to reaction of oxygen (from $UO_{2.1}$) with the reaction vessel.[35] Aitken et al.[37] identified Cs_2UO_4 and stoichiometric urania by X-ray diffraction analysis as the product of the reaction of gaseous cesium with urania pellets (initial O/U = 2.00 $^{+0.00}_{-0.00}$) held in a Mo capsule for 100 hr in a temperature gradient of 1323 to 823 K. In this experiment, Cs_2UO_4 was observed at a position corresponding to 1023 K in the thermal gradient. Adamson et al.[37,38] identified Cs_2UO_4 and stoichiometric urania by X-ray diffraction analysis as the product of the reaction of gaseous cesium $(2.5 \times 10^3$ Pa) with UO_3 powder at 1123 K (100 hr) in a Mo capsule. In simulation studies in stainless steel capsules, Aubert et al.[36] identified $Cs_2U_2O_7$ by X-ray diffraction analysis as the product of the reaction of Cs_2O with $UO_{2.00}$ at 1073 K (1500 hr) and at 1273 K (1000 hr). The diuranate, $Cs_2U_2O_7$, was also identified by X-ray diffraction analysis as the product of the reaction[36] of Cs_2O with $UO_{2.05}$ in a stainless steel capsule at 973 K (2000 hr), 1073 K (1500 hr), 1173 K (1000 hr), and 1273 K (1000 hr).

Out-of-pile experiments have also been performed with liquid cesium. Aitken et al.[37,39] reported experiments conducted in nickel capsules in which a ternary uranium(V) oxide, $Cs_{1.3}UO_3$, was in equilibrium with $UO_{2.00}$ and liquid cesium at 1073 K (100 hr). The starting materials[40] in this experiment were powdered U_3O_8 (1.2 g), Cs_2O_x (0.836 g; x = 2.5 ± 0.5), and Cs (5 g). In addition, $Cs_{1.3}UO_3$ was formed by the reaction of Cs_2UO_4 with liquid cesium in a nickel capsule at 1000 K (113 hr).[37,39] The compound $Cs_{1.3}UO_3$ was identified by chemical analysis and by a unique X-ray pattern.[40] The reported X-ray pattern for $Cs_{1.3}UO_3$ does not match the powder pattern for Cs_2UO_4 (Ref. 17), $Cs_2U_2O_7$ (Ref. 17) or

$Cs_2U_4O_{12}$ (Ref. 18). Adamson *et al.*[41] reported results obtained with an emf cell loaded with liquid cesium (5 g), Cs_2UO_4 (5 g), and stoichiometric urania (10 g). At 873 K, the initial output corresponded closely to the oxygen potential for the equilibrium:

The emf increased slowly for the next 20 hr and reached a plateau value corresponding to an oxygen potential that was 21 kJ/mol more negative than the equilibrium oxygen potential for Eq. 1. This behavior was interpreted to "constitute strong independent evidence that Cs_2UO_4(c) is converted to one or more stable Cs fuel compounds $(Cs_{0.5+x}UO_3; x = 0–0.5)$ in the presence of liquid cesium."

This review of the literature clearly indicates that some of the findings are in conflict with one another. This conflict centers about the stability of the cesium uranates formed and the conditions required for their formation. Of special interest with regard to the formation of a low-density compound at the fuel-blanket interface in uranium-oxide-blanketed mixed-oxide fuel is the identification of the cesium uranate compound or compounds that exist in equilibrium with liquid cesium and urania.

II. CESIUM-URANIUM-OXYGEN PHASE DIAGRAM

A. Estimation of Thermodynamic Properties of Cesium Uranates

To serve as a basis for the Cs-U-O phase diagram, thermodynamic functions for the cesium uranates were estimated from the measured values of the enthalpies of formation of Cs_2UO_4, $Cs_2U_2O_7$, Cs_2O, and UO_3 and the measured entropy of Cs_2UO_4, Cs_2O and UO_3 shown in Table 2. Also given in this table are enthalpy and entropy data for the reactants of the compounds listed therein. A graph was constructed (see Fig. 1) by plotting the free energy of formation of the cesium uranates from Cs_2O and UO_3 per mole of oxides (*i.e.*, moles Cs_2O plus moles UO_3) *vs.* the mole fraction of Cs_2O in the compound. The graph was drawn starting with the experimental data for the compounds Cs_2UO_4 and $Cs_2U_2O_7$, which may be written as $Cs_2O \cdot UO_3$ and $Cs_2O \cdot 2UO_3$, respectively. The value of the free energy for the next compound, $Cs_4U_5O_{17}$, was chosen so that it was about 3.2 kJ/mol less negative than that obtained by a linear extrapolation using the values for Cs_2UO_4 and $Cs_2U_2O_7$. This choice, although arbitrary in magnitude, makes the compound $Cs_2U_2O_7$ stable with respect to decomposition into Cs_2UO_4 and $Cs_4U_5O_{17}$; that is, the reaction $3Cs_2U_2O_7 = Cs_2UO_4 + Cs_4U_5O_{17}$ has a positive value for the standard free-energy change. In a similar way, free-energy values were estimated for the next compound, $Cs_2U_4O_{13}$, and for all other reported polyuranates formed by the combination of Cs_2O and UO_3.

A similar procedure was used to estimate the enthalpies of formation. Note that the ΔG_f scale in Fig. 1 is set 20 kJ higher than the ΔH_f scale. For Cs_2UO_4, the ΔH_f value in Fig. 1 is actually only 3.8 kJ more negative than the ΔG_f value. From the estimated values for the free energies and enthalpies of formation, the entropies of formation were computed. From the entropy of formation, the value of the absolute entropy for each compound was computed. The thermodynamic quantities for the compound $Cs_2U_4O_{12}$, which may also be written as $Cs_2O \cdot UO_2 \cdot 3UO_3$, were estimated from the values for $Cs_2U_4O_{13}$ by
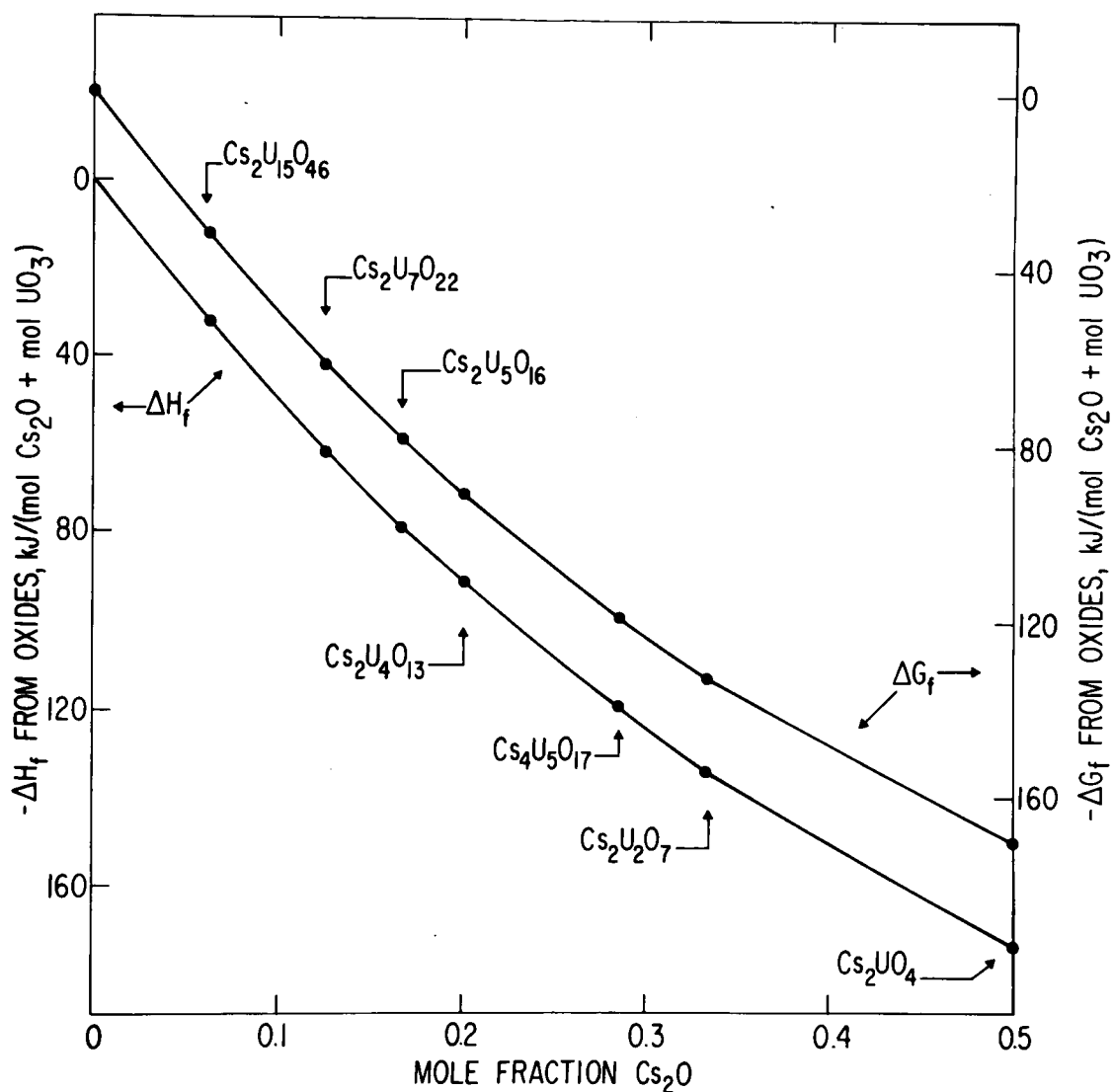
Fig. 1. Graphical Method of Estimation of
Free Energies and Enthalpies of
Formation of Cesium Uranates.

Table 2. Thermodynamic Properties of Cesium Uranates[a]

Compound	$-\Delta H_{f,298}^{\circ}$,[b] kJ/mol	$-\Delta S_{f,298}^{\circ}$, J/mol·deg	S_{298}° J/mol·deg
Cs_2UO_4	1922 ± 1.2[42,43]	411[c,d]	220 ± 0.4[44]
$Cs_2U_2O_7$	3205 ± 2.1[43,45]	656	332
$Cs_4U_5O_{17}$	7670	1560	777
$Cs_2U_4O_{12}$	5570	1090	514
$Cs_2U_4O_{13}$	5710	1170	536
$Cs_2U_5O_{16}$	6950	1430	636
$Cs_2U_6O_{18}$	8080	1630	689
$Cs_2U_7O_{22}$	9430	1940	834
$Cs_2U_9O_{27}$	11810	2400	987
$Cs_2U_{15}O_{46}$	19280	4010	1630

[a]Estimated values unless otherwise noted.
[b]Enthalpies of formation, $\Delta H_{f,298}^{\circ}$ (J/mol): Cs_2O(c), -346.0 ± 1.2 (Ref. 46);
UO_2(c), -1085 ± 0.8 (Ref. 47); $\gamma-UO_3$(c), -1228 ± 4 (Ref. 48); U_4O_9(c), -4510
(Ref. 49); U_3O_8(c), -3574 (Ref. 49).
[c]Standard entropies, S_{298}°, (J mol^{-1} deg^{-1}): Cs_2O(c), 147 ± 0.4 (Ref. 50); UO_2(c),
77.0 ± 0.02 (Ref. 19); $\gamma-UO_3$(c) 98.7 ± 0.4 (Ref. 49); U(c), 50.3 ± 0.2 (Ref. 51)
O_2(g), 205.0 ± 0.04 (Ref. 51); Cs(c), 85.1 ± 0.4 (Ref. 51); U_4O_9, 336 ± 0.4
(Ref. 49); U_3O_8, 282 ± 0.4 (Ref. 49).
[d]Additional data: ΔG_f(Cs,g) = 71,000 − 75.3 T J/mol (Ref. 52).

assuming that (1) the enthalpies of formation differ by the difference between
the enthalpies of formation of UO_3 and UO_2 and (2) that the absolute entropy
was less by the difference in entropies between UO_3 and UO_2. The values for
$Cs_2U_6O_{18}$ and $Cs_2U_9O_{27}$ were estimated in a similar manner from the thermodynamic
quantities for $Cs_2U_6O_{19}$ and $Cs_2U_9O_{28}$, respectively.[61]

B. Experimental Studies of the Reaction of Cesium with UO_{2+x}

Because of the diversity of opinion represented by the available
literature, a program was initiated to define the phase equilibria relevant to
the cesium-urania system. Our investigations included both isothermal capsule
experiments and experiments with a thermogravimetric analysis (TGA) apparatus.
The experiments involved exposure of hyperstoichiometric urania (O/U = 2.0 to
2.2) to either liquid or gaseous cesium and identification of the products by
X-ray diffraction analysis. The product in these experiments was an orange
powder that appeared to be homogeneous on visual inspection and X-ray diffraction
analysis. All operations that involved the handling of cesium and the loading
of X-ray capillaries were performed in a helium atmosphere.

In the experiments with liquid cesium, nickel capsules (7.9-mm ID, and 7 cm long) were loaded with approximately 2.5 g of powdered uranium oxide and 1.5 g of cesium and welded closed. During heat treatment over the temperature range from 873 to 1273 K, the capsule was positioned in such a way that only liquid cesium was in contact with the uranium oxide. At the end of the heat treatment, the capsule was quickly quenched (15 s) and the excess cesium removed by vacuum distillation at 573 K.

To study the reaction of gaseous cesium with uranium oxide, a Type 304 stainless steel capsule (2.5-cm ID, and 18 cm long) was loaded with a nickel tray containing 1.5 g of powdered uranium oxide and a separate nickel tray containing 5 g of cesium and welded closed. During heat treatment, the capsule was positioned so that only gaseous cesium contacted the uranium oxide. The gaseous cesium pressure was calculated[52] from the temperature (600 K) at the coolest portion of the capsule, one end of which was maintained in a temperature gradient. The tray containing uranium oxide was in an isothermal zone at 1073 K.

In the TGA apparatus, powdered uranium oxide was exposed to gaseous cesium in a helium gas stream which had a 2 Pa H_2O impurity level and an oxygen potential of -364 kJ/mol at 1073 K maintained by an Fe/FeO buffer. The oxygen potential of the gas stream was measured with a calibrated emf cell having a sensor of yttria-stabilized zirconia.

The experimental conditions and the results of our experiments are summarized in Table 3. The normal cesium uranate, Cs_2UO_4, and "stoichiometric" uranium dioxide (a = 5.470 x 10^{-10} m) were identified by X-ray diffraction analysis in all cases. The X-ray data are shown in Tables 4 and 5 in the form of experimental d values which may be compared to similar literature data in Table 4 for UO_2, Cs_2UO_4, $Cs_2U_2O_7$ and $Cs_2U_4O_{12}$. The relative intensities (I/I_o) of the strongest lines in the X-ray diffraction pattern of UO_2, Cs_2UO_4, $Cs_2U_2O_7$ and $Cs_2U_4O_{12}$ are listed to show that the lines which we observed experimentally correspond to the most intense X-ray diffraction lines of Cs_2UO_4. In the TGA experiments, the kinetics of the reaction of gaseous cesium with powdered UO_{2+x} indicated that the reaction proceeded as shown in Eq. 2:

$$xCs(g) + UO_{2+x} \rightarrow \frac{2-x}{2} UO_2 + \frac{x}{2} Cs_2UO_4 \qquad (2)$$
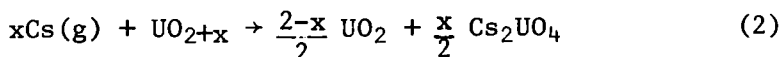
All the excess oxygen in the urania (x in UO_{2+x}) was consumed by reaction 2 in the first seven hours, whereupon the reaction ceased.

Our results clearly show that a hexavalent cesium uranate, Cs_2UO_4, is the Cs-U-O phase in equilibrium with liquid cesium and urania in the temperature range from 873 to 1273 K. This conflicts with the results of Aitken et al.[37,39,40] and Adamson[41] who reported that Cs-U-O compounds with a net uranium valence of less than 6, $Cs_{1.3}UO_3$ or $Cs_{0.5+x}UO_3$ (x = 0-0.5), existed in equilibrium with liquid cesium and urania in the temperature range from 873 to 1073 K. Our results are consistent with the results of Efremova,[22] Rudorff et al.,[24,25] Cordfunke et al.,[17] and van Egmond[18,29-31] in that the pentavalent uranate, $CsUO_3$, does not exist in the Cs-U-O system. Moreover, our results clearly show that a hexavalent cesium uranate, Cs_2UO_4, can exist in equilibrium with gaseous cesium and urania at 1073 K. Our result is supported by the results

Table 3. Summary of Experimental Results for Reaction of Cesium with Uranium Oxide.

Expt. No.	Type of Experiment	Cesium Pressure, Pa	Uranium Oxide Temp., K	Initial O/U Atom Ratio of Uranium Oxide	Time at Temp., hr	Product Phases Identified By X-ray Diffraction
1	Ni capsule	a	873	2.004	161	Cs_2UO_4 + stoichio-metric uranium di-oxide
2	Ni capsule	a	873	2.068	150	
3	Ni capsule	a	1073	2.20	280	
4	Ni capsule	a	1273	2.20	280	
5	SS capsule	5×10^2	1073	2.1	393	
6	TGA	1×10^2	1073	2.04	7	
7	TGA	5×10^4	1073	2.07	5.5	

[a]Uranium oxide sample in contact with liquid cesium.

Table 4. X-Ray Data for Several Cesium Uranates

d,Å	I/I$_o$					Experimental d Values[a]						
	UO$_2$ (Ref. 53)	Cs$_2$UO$_4$ (Ref. 17)	β-Cs$_2$U$_2$O$_7$ (Ref. 17)	α-Cs$_2$U$_4$O$_{12}$ (Ref. 18)	γ-Cs$_2$U$_4$O$_{12}$ (Ref. 18)	Expt. No. 1[b] (8547)[c]	Expt. No. 2 (8318)	Expt. No. 3 (9020)	Expt. No. 4 (8844)	Expt. No. 5 (8694)	Expt. No. 6 (8525)	Expt. No. 7 (7478R)
7.356±1		23										
6.922			41									
6.482					38							
6.387				26								
6.311				65								
3.970±.02					8							3.46
3.727			70									
3.459			68									
3.385					100							
3.350			68									
3.333			55									
3.328				62								
3.301				77								
3.291				62		3.25	3.25	3.27	3.27	3.29	3.28	3.26
3.276		100										
3.241					54							
3.197				42								
3.165			100									
3.157	100											
3.153				100		3.08	3.10			3.10	3.09	3.09
3.101		37										
3.087			55					2.81	2.85			
2.739±.010				22								
2.735	48					2.45	2.45		2.46	2.46	2.48	2.46
2.466		8										
2.412			20			2.18	2.18		2.19	2.19	2.20	2.19
2.194		18										
2.160					26							
2.154			25									2.14
2.108				25								
(Con't)												

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Table 4. (Con't)

d,Å	I/I_o					Experimental d Values[a]						
	UO_2 (Ref. 53)	Cs_2UO_4 (Ref. 17)	β-$Cs_2U_2O_7$ (Ref. 17)	α-$Cs_2U_4O_{12}$ (Ref. 18)	γ-$Cs_2U_4O_{12}$ (Ref. 18)	Expt. No. 1[b] (8547)[c]	Expt. No. 2 (8318)	Expt. No. 3 (9020)	Expt. No. 4 (8844)	Expt. No. 5 (8694)	Expt. No. 6 (8525)	Expt. No. 7 (7478R)
2.102				31	29			1.99				
1.984												
1.934	49											
1.932		22			13							
1.897												
1.854			26			1.82	1.82		1.84	1.83	1.82	1.82
1.824		29			23							
1.693												
1.649	47								1.54			
1.639		19										
1.579±.004	13											
1.462					12	1.39			1.40	1.405		
1.403		8							1.365	1.39		
1.35			25							1.26		
1.261		7										
1.255	18											
1.223	15									1.21		
1.210		5									1.215	
1.204		4										
1.116	13											
1.052	15											
0.924±002	15											

[a] In addition to urania lines.

[b] See Table 2 for experimental conditions.

[c] X-ray film number.

Table 5. Complete X-Ray Diffraction
Data for Experiment 5

Cs_2UO_4 d Values (Ref. 17)	I/I_o (Ref. 17)	Expt'l d Values[a]
7.356	23	-
3.276	100	3.29
3.101	37	3.10
2.863	1	
2.466	8	2.46
2.194	18	2.19
2.104	2	
1.945	2	
1.932	22	1.93[b]
1.8506	3	
1.824	29	1.83
1.639	19	1.65
1.588	2	1.58
1.552	7	1.55 - 1.54
1.5196	1	
1.4145	2	
1.403	8	1.40
1.389	6	1.39
1.314	6	1.315
1.261	7	1.26
1.234	1	
1.228	1	1.225[b]
1.210	4	1.211
1.204	5	1.118

[a]See Table 2 for experimental conditions.

[b]Coincide with UO_2 lines.

of Aubert *et al.*[36] Venker *et al.*,[34] Aitken *et al.*,[37] and Adamson *et al.*,[38] who showed that $Cs_2U_2O_7$ (973 to 1273 K), $Cs_2UO_4/Cs_2U_2O_7$ (973 K), Cs_2UO_4 (1073 K), and Cs_2UO_4 (1123 K), respectively, exist in equilibrium with gaseous cesium and urania. However, our result is in conflict with the finding of Cordfunke[33] that only $Cs_2U_4O_{12}$ (with a net uranium valency of less than 6) exists in equilibrium with gaseous cesium and urania at temperatures above 873 K.

The experimental results and the thermodynamic data on cesium uranates obtained in this laboratory and the experimental data of Venker *et al.*,[34] Aubert *et al.*,[36] Cordfunke *et al.*,[17,33] van Egmond,[18,29-31] Aitken *et al.*,[37] and Adamson *et al.*,[38] were used to construct the phase diagrams shown in Figs. 2 and 3. Specifically, our results and the data of Venker *et al.*,[34] Aitken *et al.*,[37] and Adamson *et al.*[38] were used to construct the Cs_2UO_4-UO_{2+x} tie line. The data of Aubert *et al.*[36] was used to construct the $Cs_2U_2O_7$-UO_{2+x} tie line. The $Cs_2U_4O_{12}$-UO_{2+x} tie line and remaining tie lines in Fig. 3 were based on the results of Cordfunke *et al.*[17,33] and van Egmond.[18,29-31]

Figures 2 and 3 represent isothermal sections over the temperature range from 873 to 1273 K. The Cs-UO_{2+x} and Cs-Cs_2UO_4 tie lines exist[52] only below 950 K. The Cs_2UO_4-UO_{2+x}, $Cs_2U_2O_7$-UO_{2+x}, and $Cs_2U_4O_{12}$-UO_{2+x} tie lines exist over the range from 873 to 1273 K. The widths of these two-phase regions vary with temperature. Phase regions containing cesium uranates with a higher U/Cs atom ratio than that of $Cs_2U_4O_{12}$ may not exist over the entire temperature range from 873 to 1273 K. Uranium trioxide, UO_3, exists only below 930 K.[48] At temperatures above 873 K, $Cs_2U_4O_{13}$ and $Cs_2U_5O_{16}$ form a solid solution.[17,29]

There are three key features related to Figs. 2 and 3. Firstly, the experimental data of Cordfunke *et al.*[17] clearly establish a $Cs_2U_4O_{12}$-U_3O_8 tie line. The $Cs_2U_4O_{12}$-U_3O_8 tie line is consistent with the thermodynamic properties shown in Table 2. The existence of a $Cs_2U_4O_{12}$-U_3O_8 tie line indicates that there can be no tie line between UO_{2+x} and a cesium uranate with a higher U/Cs atom ratio than that of $Cs_2U_4O_{12}$. Secondly, only three of the ten ternary cesium-uranium-oxygen compounds (Cs_2UO_4, $Cs_2U_2O_7$, $Cs_2U_4O_{12}$) exist in equilibrium with UO_{2+x}. Consequently, the cesium uranate which forms at the fuel-blanket interface (where UO_{2+x} is always present in excess) must be either Cs_2UO_4, $Cs_2U_2O_7$, or $Cs_2U_4O_{12}$. Thirdly, Cs_2UO_4 is the compound which exists in equilibrium with liquid cesium and urania. Consequently, cesium analogs (which have not been observed to date) of pentavalent uranates such as $NaUO_3$[23,54] and Na_3UO_4[23,54] do not exist in equilibrium with UO_{2+x}. If either of these cesium analogs existed in the temperature range 873 to 1273 K, it would exist in equilibrium with liquid cesium and urania.

C. Calculation of Phase Equilibria

By application of the phase rule, it can be shown that in the three-phase regions shown in Figs. 2 and 3 (*e.g.*, Cs_2UO_4-$Cs_2U_2O_7$-UO_2), there is one degree of freedom; therefore, setting the temperature fixes the cesium partial pressure and the oxygen partial pressure of the system. On the other hand, along the two-phase tie lines (*e.g.*, the Cs_2UO_4-UO_{2+x} tie line), there are two degrees of freedom; therefore, at a set temperature, the cesium partial pressure depends on the oxygen partial pressure of the system. The dependency of the cesium partial pressure on the oxygen partial pressure at Cs-U-O compositions falling on the two-phase tie lines can be calculated from the
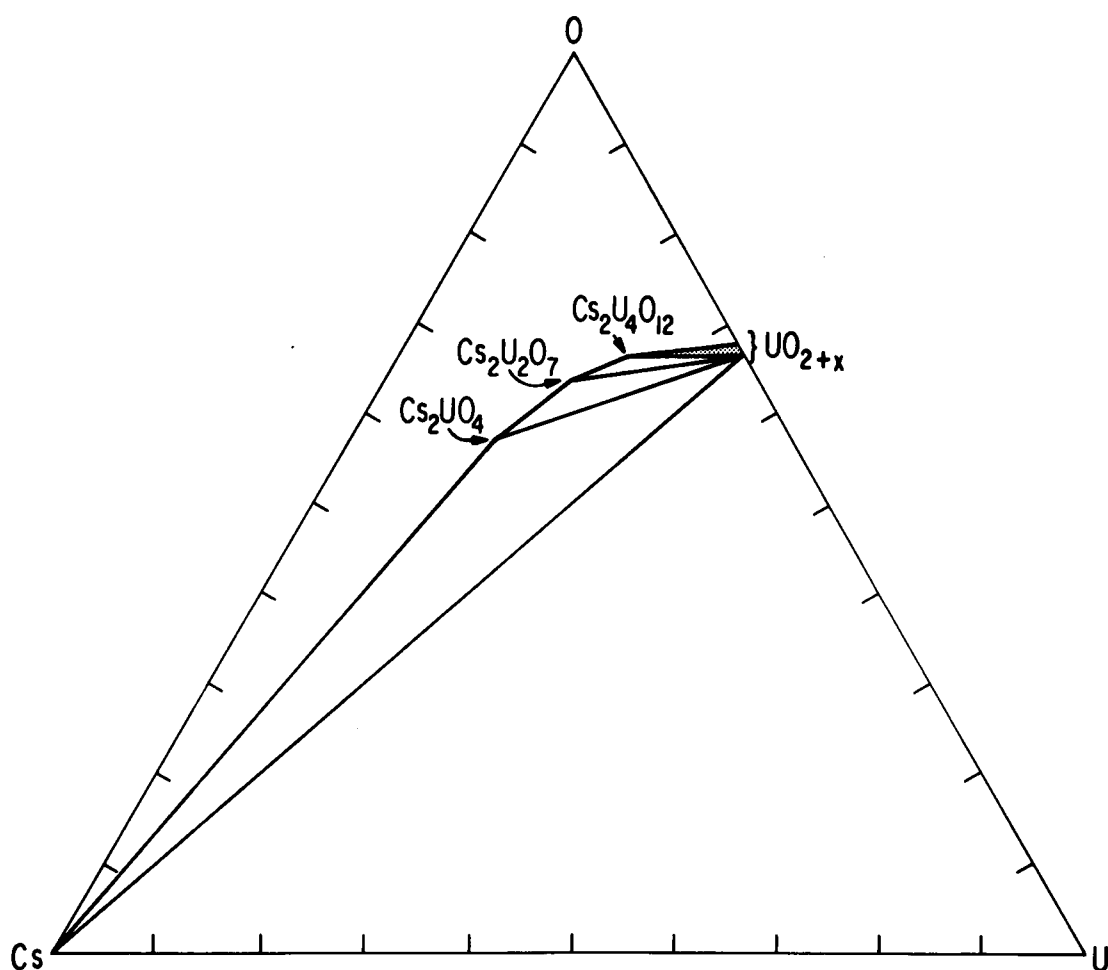
Fig. 2. Selected Portions of the Cesium–Uranium–Oxygen Phase
Diagram Showing Tie Lines to UO_{2+x}; Isothermal Sections
from 873 to 1273 K. (The solid area shows the extent
of the two-phase region at 873 K. The Cs–UO_{2+x} and
Cs–Cs_2UO_4 tie lines exist[52] only below 950 K.)
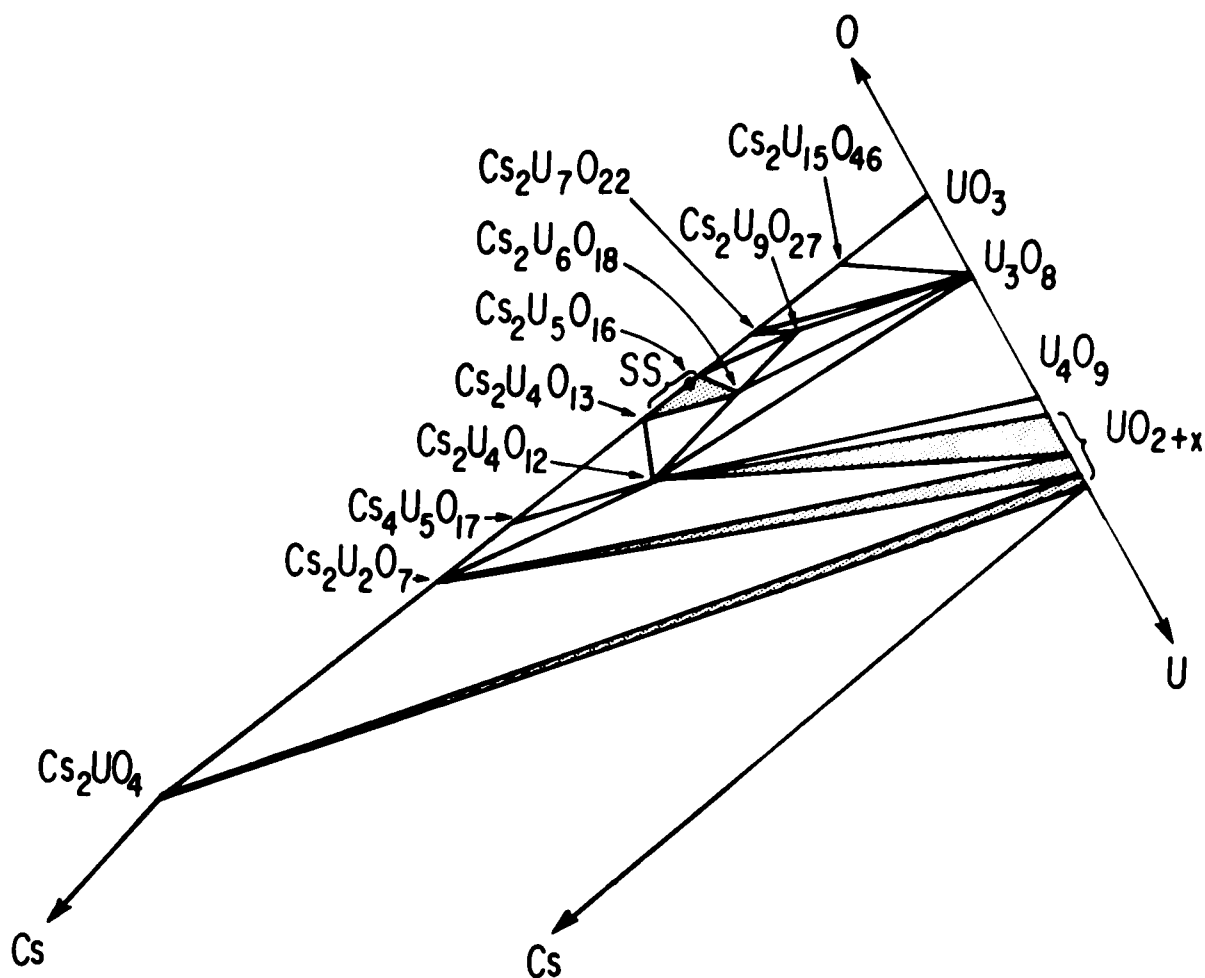
Fig. 3. Selected Portions of the Cesium–Uranium–Oxygen Phase Diagram; Isothermal Sections from 873 to 1273 K. (The solid areas show the width of two-phase regions at 1273 K. The compound UO_3 exists[48] only below 930 K. The $Cs-UO_{2+x}$ and $Cs-Cs_2UO_4$ tie lines exist[52] only below 950 K. Phase regions containing cesium uranates with a higher U/Cs atom ratio than $Cs_2U_4O_{12}$ may not exist over the entire temperature range; see text. SS = $Cs_2U_4O_{13}-Cs_2U_5O_{16}$ solid solution.[17,29])

measured thermodynamic properties of the phases present. The fixed cesium partial pressure and the fixed oxygen partial pressure in the three-phase regions can be calculated in a similar manner.

Consider the equilibrium

$$2Cs(g) + UO_2(c) + O_2(g) \rightleftarrows Cs_2UO_4(c) \tag{3}$$
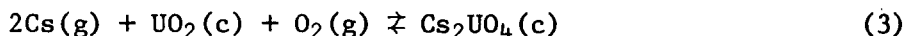
which exists along the $Cs_2UO_4-UO_{2+x}$ tie line. The corresponding free energy relationship may be written as follows:

$$\Delta G_f^o(Cs_2UO_4,c) - 2\Delta G_f^o(Cs,g) - 2RT \ln P_{Cs} - \Delta G_f^o(UO_2,c) - RT \ln p_{O_2} = 0 \tag{4}$$

The cesium pressure and the oxygen potential ($\Delta\bar{G}_{O_2} = RT \ln p_{O_2}$) are related by

$$\ln P_{Cs} = [\Delta G_f^o(Cs_2UO_4,c) - 2\Delta G_f^o(Cs,g) - \Delta G_f^o(UO_2,c) - \Delta\bar{G}_{O_2}]/2RT \tag{5}$$

Similar expressions can be derived to relate the cesium pressure and the oxygen potential on the $Cs_2U_2O_7-UO_{2+x}$ tie line and on the $Cs_2U_4O_{12}-UO_{2+x}$ tie line. The calculated cesium pressures are shown in Fig. 4; these are based on the thermodynamic data from Table 2, with the assumption that ΔH_f^o and ΔS_f^o are independent of temperature. This approach is valid for Cs_2UO_4 on the basis of the known high-temperature thermodynamic properties of this compound.[55] The effect on the thermodynamic properties of the $\alpha \rightarrow \beta$ phase transition[17] of $Cs_2U_2O_7$ at 573 K and the $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ phase transitions[33] of $Cs_2U_4O_{12}$ at 898 and 968 K, respectively, is assumed to be small and has been neglected. This assumption has been shown to be valid in other ternary oxide systems.[52]

Another assumption in the calculation of the cesium pressures shown in Fig. 4 is that the solubility of cesium in urania or in the cesium uranates does not significantly affect the thermodynamic properties shown in Table 2. This assumption appears to be valid. The measured[56] solubility of cesium in a $(U,Pu)O_2$ matrix is less than 1 ppm. A similar solubility of cesium in UO_{2+x} would not affect the equilibrium oxygen pressure over the UO_{2+x} even if the deviations from Raoult's law were large.

The estimated thermodynamic values for $Cs_2U_4O_{12}$ shown in Table 2 are used in this paper instead of values derived from Cordfunke's emf measurements.[33] The data of Venker et al.,[34] Aubert et al.,[36] Aitken et al.,[37] Adamson et al.,[38] and this work showing that Cs_2UO_4 and $Cs_2U_2O_7$ exist in equilibrium with UO_{2+x} above 873 K demonstrate the inadequacy of Cordfunke's emf measurements[33] in obtaining the thermodynamic properties of $Cs_2U_4O_{12}$. According to Cordfunke's emf data, with an oxygen potential that is more negative than -170 kJ/mol, $Cs_2U_4O_{12}$ is the only possible cesium uranate in equilibrium with UO_{2+x} in the temperature range of Cordfunke's experiments, 974-1024 K.

In Fig. 4, consider the 1273 K values. At lower oxygen potentials ($\Delta\bar{G}_{O_2}$ more negative than -230 kJ/mol), the $Cs_2UO_4-UO_{2+x}$ region has the lowest equilibrium cesium pressure and is thus the only stable two-phase region at these oxygen potentials. Solid lines and solid symbols in Fig. 4 indicate the stable two-phase regions at each oxygen potential. Dashed lines and open symbols indicate the calculated equilibrium cesium pressure even though the corresponding two-phase region does not exist at that oxygen potential. As

Fig. 4. Cesium Equilibrium Pressure over Two-Phase Regions in Cs-U-O Phase Diagram. (Solid lines and solid symbols indicate the stable phases at each oxygen potential and the range of stability for each of the two-phase regions considered. Dashed lines and open symbols indicate the calculated cesium equilibrium pressure, even though the corresponding two-phas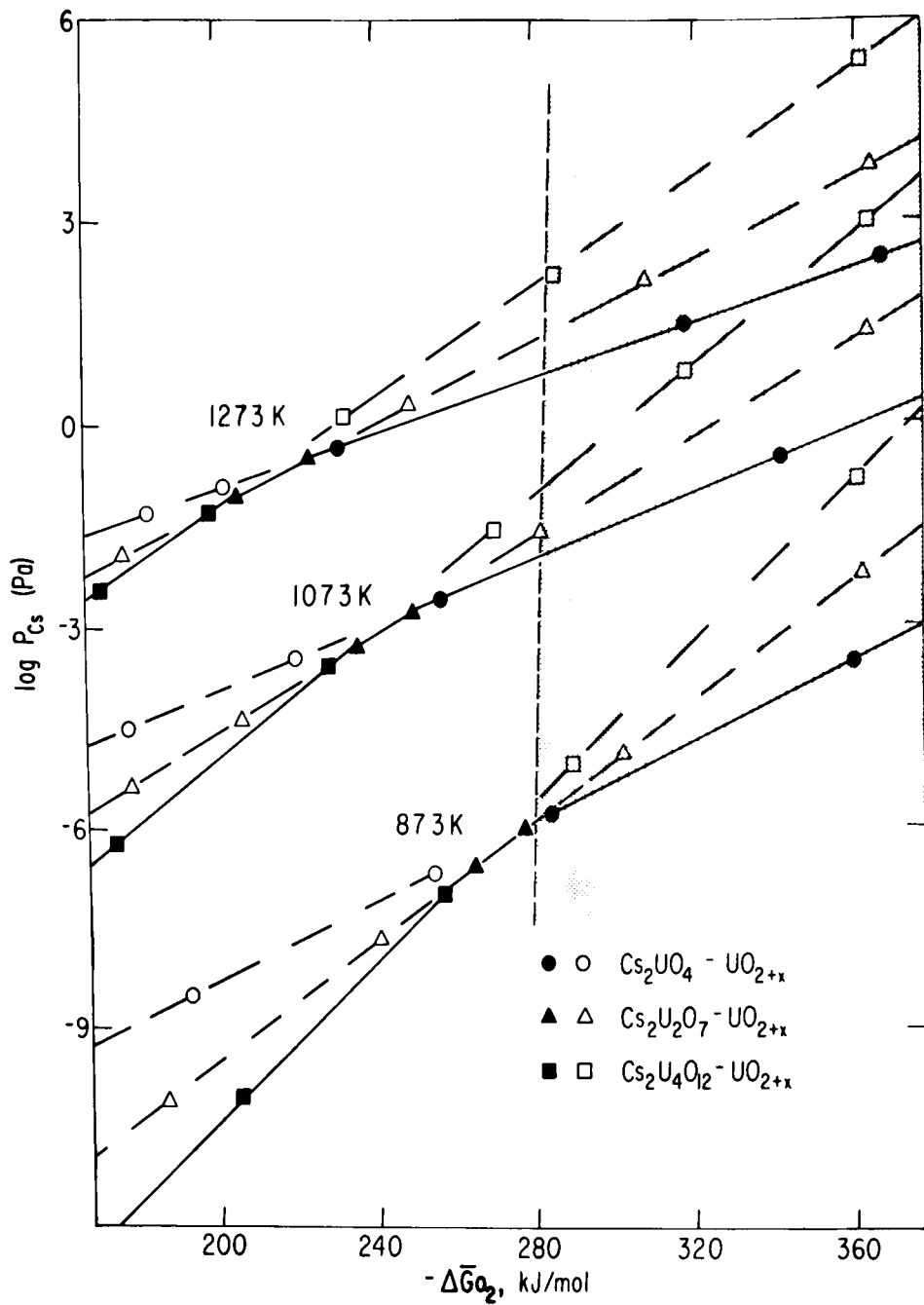e region does not exist at that oxygen potential. The gray area corresponds to oxygen potentials[20] more negative than the oxygen potential of $UO_{2.002}$.)

the oxygen potential over the Cs_2UO_4-UO_{2+x} region becomes more positive, the cesium equilibrium pressure decreases. At a unique oxygen potential (-225 kJ/mol at 1273 K), the cesium pressure over the Cs_2UO_4-UO_{2+x} region is the same as the cesium pressure over the $Cs_2U_2O_7$-UO_{2+x} region [log P_{Cs}(Pa) = -0.5]. This point is the intersection of the lines in Fig. 4 labeled Cs_2UO_4-UO_{2+x} and $Cs_2U_2O_7$-UO_{2+x} and represents the oxygen potential and cesium pressure of the Cs_2UO_4-$Cs_2U_2O_7$-UO_{2+x} region at 1273 K. At oxygen potentials slightly more positive than -225 kJ, the $Cs_2U_2O_7$-UO_{2+x} region has the lowest cesium equilibrium pressure. The $Cs_2U_2O_7$-UO_{2+x} region is thus the only stable two-phase region at these oxygen potentials.

As the oxygen potential over the $Cs_2U_2O_7$-UO_{2+x} region becomes more positive, the cesium equilibrium pressure decreases. At a unique oxygen potential (-202 kJ/mol at 1273 K), the cesium pressure over the $Cs_2U_2O_7$-UO_{2+x} region is the same as the cesium pressure over the $Cs_2U_4O_{12}$-UO_{2+x} region [log P_{Cs} (Pa) = -1.2]. This point is the intersection of the lines labeled $Cs_2U_2O_7$-UO_{2+x} and $Cs_2U_4O_{12}$-UO_{2+x} and is the oxygen potential and cesium pressure of the $Cs_2U_2O_7$-$Cs_2U_4O_{12}$-UO_{2+x} region at 1273 K. At oxygen potentials more positive than -202 kJ/mol, the $Cs_2U_4O_{12}$-UO_{2+x} region has the lowest cesium equilibrium pressure. The $Cs_2U_4O_{12}$-UO_{2+x} region is thus the only stable two-phase region at these oxygen potentials.

The three stable two-phase regions in Fig. 4 (Cs_2UO_4-UO_{2+x}, $Cs_2U_2O_7$-UO_{2+x}, and $Cs_2U_4O_{12}$-UO_{2+x}) are shown as tie lines in the Cs-U-O phase diagrams in Figs. 2 and 3. The other tie lines in Fig. 3 can be constructed in a similar manner from the thermodynamic data in Table 2. The absence of possible tie lines can also be inferred from thermodynamic considerations. For example, no $Cs_4U_5O_{17}$-UO_{2+x} tie line exists because thermodynamic calculations show that there is no stable $Cs_4U_5O_{17}$-UO_{2+x} region (*i.e.*, the calculated cesium equilibrium pressure over the hypothetical $Cs_4U_5O_{17}$-UO_{2+x} region is not the lowest cesium equilibrium pressure for any oxygen potential or temperature shown in Fig. 4).

In a fashion similar to the foregoing, the oxygen potentials and cesium pressures over the three-phase regions shown in Figs. 2 and 3 may be obtained. For example, the oxygen potential of the Cs_2UO_4-$Cs_2U_2O_7$-UO_{2+x} region may be calculated from the thermodynamic relationship associated with the equilibrium

$$Cs_2UO_4(c) + UO_2(c) + 1/2 \ O_2(g) \rightleftharpoons Cs_2U_2O_7(c) \qquad (6)$$
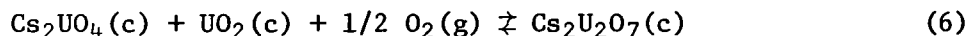
The oxygen potentials and cesium pressures over selected three-phase regions shown in Figs. 2 and 3 are given in Table 6; these were derived using the data from Table 2. As shown in Table 6, the oxygen potential of the Cs_2UO_4-$Cs_2U_2O_7$-UO_{2+x} region at 1273 K corresponds[20] to $UO_{2.03}$. Therefore, the thermodynamic relationship associated with the equilibrium

$$Cs_2UO_4(c) + UO_{2+x}(c) + \frac{1-x}{2} \ O_2(g) = Cs_2U_2O_7(c) \qquad (7)$$
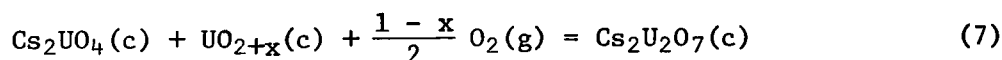
and the thermodynamic data[49] for UO_{2+x} (instead of UO_2) should be used. However, the data in Table 6 have not been corrected for the deviations in stoichiometry of urania because these corrections are less than ±4 kJ/mol, which is within the uncertainty of the estimated thermodynamic values for cesium uranates.

Table 6. Calculated Oxygen Potentials (kJ/mol) and Cesium
Pressures (Pa) at Selected Temperatures in Three-
Phase Regions of the Cs-U-O Phase Diagram

Region	873 K		1073 K		1273 K	
	$-\log P_{Cs}$	$-\Delta \bar{G}_{O_2}$	$-\log P_{Cs}$	$-\Delta \bar{G}_{O_2}$	$-\log P_{Cs}$	$-\Delta \bar{G}_{O_2}$
$Cs(\ell) + Cs_2UO_4 + UO_{2+x}$	–	633	–	587	–	541
$Cs_2UO_4 + Cs_2U_2O_7 + UO_{2+x}$	5.9	280	2.7	251	0.5	225
$Cs_2U_2O_7 + Cs_2U_4O_{12} + UO_{2+x}$	6.7	261	2.8	231	1.2	202
$Cs_2U_4O_{12} + U_4O_9 + UO_{2+x}$ (a)	9.4	217	5.6	187	3.4	146
$Cs_2U_4O_{12} + U_4O_9 + U_3O_8$ (a)	11.4	176	7.3	146	4.4	117
$Cs_2U_4O_{12} + Cs_2U_6O_{18} + U_3O_8$	11.5	175	7.7	127	5.0	78
$Cs_2U_6O_{18} + Cs_2U_9O_{27} + U_3O_8$	12.4	147	8.0	112	5.0	77
$Cs_2U_9O_{27} + Cs_2U_7O_{22} + U_3O_8$	15.7	72[b]	9.4	74	5.1	76
$Cs_2U_7O_{22} + Cs_2U_{15}O_{46} + U_3O_8$	15.2	82[b]	10.5	47	7.3	12

[a] The oxygen potential in this three-phase region is the oxygen potential of
the U_4O_{9-y}-UO_{2+x} or U_4O_9-U_3O_{8-z} two-phase region (Ref. 49), assuming no
effect from cesium solubility. The oxygen potential is independent of the
estimated thermodynamic properties of $Cs_2U_4O_{12}$; the cesium pressure depends
on the estimated thermodynamic properties of $Cs_2U_4O_{12}$ in these three-phase
regions.

[b] Not a stable three-phase region at this temperature. The stable three-phase
region at 873 K is $Cs_2U_9O_{27}$-$Cs_2U_{15}O_{46}$-U_3O_8, with $\Delta \bar{G}_{O_2}$ = -81 kJ/mol and
log P_{Cs} = -15.3.

D.   Accuracy of Calculated Phase Equilibria

     The data in Table 6 are in accord with the experimental phase diagram.
At a given temperature, the oxygen potential becomes more positive and the
cesium pressure decreases going from top to bottom in the table. Furthermore,
the estimated thermodynamic data predict the observed tie lines[33] between U_3O_8
and $Cs_2U_4O_{12}$, $Cs_2U_4O_{12}$, $Cs_2U_6O_{18}$, $Cs_2U_9O_{27}$ and $Cs_2U_7O_{22}$ and the absence of a
tie line between U_3O_8 and $Cs_2U_5O_{16}$ and between U_3O_8 and $Cs_2U_4O_{13}$. However,
the set of thermodynamic data that predicts the observed tie lines to U_3O_8 is
not unique and a slightly altered set would result in the same ordering of the
oxygen potentials and predictions of tie lines. Therefore, while it appears
that the estimated thermodynamic data in Table 2 are qualitatively correct,
the quantitative accuracy of the data in Table 2 is uncertain and requires
further experimentation.

In view of the lack of high-temperature thermodynamic measurements on most cesium uranates, the validity of the data in Table 6 is naturally subject to question. The data for the $Cs(\ell) + Cs_2UO_4 + UO_{2+x}$ region have the least uncertainty because reliable high-temperature thermodynamic data are available for Cs_2UO_4[55] and UO_2.[57] The data for the Cs_2UO_4-$Cs_2U_2O_7$-UO_{2+x} region were calculated using enthalpy measurements (at 298 K) and estimated entropy data for $Cs_2U_2O_7$. An uncertainty of ±8 J/mol·deg in the entropy estimate becomes an uncertainty of ±8 kJ/mol in the calculated oxygen potential of the $Cs_2U_2O_7$-Cs_2UO_4-UO_{2+x} region. The uncertainty in the calculated oxygen potential of the three-phase regions which lie below the Cs_2UO_4-$Cs_2U_2O_7$-UO_{2+x} region in Table 6 is greater than ±8 kJ/mol and increases going down the table owing to the increasing uncertainty in the extrapolation technique shown in Fig. 1.

A lower limit for the oxygen potential in the three-phase regions containing cesium uranates with U/Cs atom ratios higher than that of $Cs_2U_2O_7$ can be established within an uncertainty of ±8 kJ/mol because of the following considerations. The lower limit is given by the intersection of the solid lines labeled Cs_2UO_4-UO_{2+x} and $Cs_2U_2O_7$-UO_{2+x} in Fig. 4. (The evidence for the existence of these two-phase regions has been previously discussed.) Consequently, in Fig. 4, lines corresponding to stable cesium uranates with a U/Cs atom ratio higher than $Cs_2U_2O_7$ can intersect the Cs_2UO_7-UO_{2+x} line *only* at oxygen potentials more positive than that at the intersection of the $Cs_2U_2O_7$-UO_{2+x} line and the Cs_2UO_4-UO_{2+x} line. The lower limit for the oxygen potential of three-phase regions containing cesium uranates with U/Cs atom ratios higher than that of $Cs_2U_2O_7$ is therefore the oxygen potential of the Cs_2UO_4-$Cs_2U_2O_7$-UO_{2+x} field.

The phase equilibria shown in Figs. 2 and 3 and Table 6 may also be inaccurate in that all ten cesium uranates are shown to exist in the temperature range from 873 to 1273 K. The results of this study, as well as those of Aubert *et al.*[36] and Cordfunke,[17,33] show that the Cs_2UO_4-UO_{2+x}, $Cs_2U_2O_7$-UO_{2+x}, and $Cs_2U_4O_{12}$-UO_{2+x} regions exist in the stated temperature range. In Fig. 3, regions containing U_3O_8 may not exist over the entire range of 873–1273 K. Cordfunke's psudeo-binary Cs-U-O phase diagram[17] at $P_{O_2} = 2 \times 10^4$ Pa shows that the transitions $Cs_2U_{15}O_{46}$-$U_3O_8 \rightarrow Cs_2U_9O_{27}$-$U_3O_8 \rightarrow Cs_2U_4O_{12}$-$U_3O_8$ occur with increasing temperature. Cordfunke concludes that the $Cs_2U_4O_{12}$-U_3O_8 region is the only stable two-phase region containing U_3O_8 at high temperatures. In contrast to Cordfunke's conclusion, we assert that all of these two-phase regions may exist at the highest temperature reached. As shown in Fig. 4, at $P_{O_2} = 2 \times 10^{-7}$ Pa, the stable two-phase regions are $Cs_2U_4O_{12}$-UO_{2+x} at 873 K (-195 kJ/mol); $Cs_2U_2O_7$-UO_{2+x} at 1073 K (-240 kJ/mol); and Cs_2UO_4-UO_{2+x} at 1273 K (-285 kJ/mol). Experimentally, at a fixed P_{O_2} of 2×10^{-7} Pa, the transitions $Cs_2U_4O_{12}$-$UO_{2+x} \rightarrow Cs_2U_2O_7$-$UO_{2+x} \rightarrow Cs_2UO_4$-$UO_{2+x}$ would be observed during a temperature increase from 873 K to 1273 K. A similar ordering of the temperature and oxygen potential conditions for stable two-phase regions containing U_3O_8 may account for Cordfunke's observations. Consequently, in Fig. 3, phase regions containing U_3O_8 are shown to be unaffected by temperature in the range 873 to 1273 K because there are neither experimental thermodynamic data nor experimental phase data at a sufficient number of oxygen potentials to warrant our doing otherwise.

III. APPLICATION TO URANIUM-PLUTONIUM OXIDE FUEL PINS

The range of oxygen potentials of the urania blanket pellets prior to irradiation is shown as the gray area in Fig. 4. As shown in Table 6 and Fig. 4, at 1273 K, an oxygen potential more positive than -225 kJ/mol (corresponding to $UO_{2.03}$[20]) is required to form any cesium uranate other than Cs_2UO_4. Similarly, at 1073 K, an oxygen potential more positive than -251 kJ/mol (corresponding to $UO_{2.01}$[20]) is required to form any cesium uranate other than Cs_2UO_4. These high oxygen potentials are not likely to be encountered at the fuel-blanket interface for uranium oxide blanket pellets that are initially near stoichiometric composition. At 873 K, an oxygen potential more positive than -280 kJ/mol (corresponding to $UO_{2.002}$[20]) would be required to form a cesium uranate other than Cs_2UO_4. The accuracy of the determination[58,59] of the O/U ratio in the uranium oxide blanket pellets is ±0.002. Thus $UO_{2.002}$ blanket pellets might be loaded into a fuel pin in place of the specified stoichiometric uranium dioxide. When a fuel pin is brought to power, oxygen is expected to migrate across the fuel-blanket interface from the blanket to the fuel.[60] (The more negative oxygen potential encountered in going from the blanket to the fuel is the driving force for this solid-state diffusion of oxygen.) A small migration of oxygen is sufficient to substantially lower the oxygen potential of the blanket pellet. For example, the oxygen potential of $UO_{2.001}$ is -290 kJ/mol at 873 K.[20] The oxygen potential of the uranium oxide at the fuel-blanket interface is further lowered by the consumption of oxygen in forming any cesium uranate. The solid-state diffusion of oxygen from the blanket to the fuel and the consumption of oxygen in forming any cesium uranate are expected to lower the oxygen potential of the blanket pellet to the point where Cs_2UO_4 is the only stable cesium uranate (even with the ±8 kJ uncertainty in the oxygen potential of the Cs_2UO_4-$Cs_2U_2O_7$-UO_{2+x} region). No evidence was found in our kinetic studies to indicate kinetic constraints on Cs_2UO_4 formation. Therefore, we conclude that the normal cesium uranate, Cs_2UO_4, is the only Cs-U-O compound expected to be formed at temperatures of 873 K or higher in the uranium oxide blanket at the interface between the mixed-oxide fuel and the blanket in irradiated fast reactor fuel pins.

This conclusion differs from Cordfunke's[33] because our studies were directed toward more negative oxygen potentials. Cordfunke's experiments were performed at a much higher oxygen potential ($p_{O_2} \leq 10^{-5}$ Pa) than encountered in the fuel pins. As shown in Figs. 3 and 4 and Table 6, we concur with Cordfunke that the $Cs_2U_4O_{12}$-UO_{2+x} two-phase region is stable at higher oxygen potentials. The stability of the $Cs_2U_4O_{12}$-UO_{2+x} region over a wide range of oxygen potentials (-261 to -217 kJ/mol at 873 K, as shown in Table 6, for example) explains why Cordfunke observed $Cs_2U_4O_{12}$-UO_{2+x} in experiments at $P_{O_2} \leq 10^{-5}$ Pa with widely varying initial Cs-U-O compositions.

In addition, the conclusion in our work that Cs_2UO_4 is the only Cs-U-O compound that forms in the uranium oxide blanket at the fuel-blanket interface differs from the findings of Cordfunke[33] because in our work the stabilities of regions containing UO_{2+x} were compared. These comparisons were made because the UO_{2+x} phase is always present at the fuel-blanket interface. At $P_{O_2} \leq 10^{-5}$ Pa, Cordfunke concluded that $Cs_2U_4O_{12}$, not Cs_2UO_4 or $Cs_2U_2O_7$, would form by observing the decomposition sequence $Cs_2UO_4 \rightarrow Cs_2U_2O_7 \rightarrow Cs_2U_4O_{12} + UO_2$. Only $Cs_2U_4O_{12}$ existed in a two-phase region with UO_{2+x}. Cordfunke thus compared relative stabilities along the Cs_2UO_4-$Cs_2U_2O_7$, $Cs_2U_2O_7$-$Cs_2U_4O_{12}$ and $Cs_2U_4O_{12}$-UO_{2+x}

two-phase regions (see tie lines in Fig. 3). We have compared the stabilities in the Cs_2UO_4-UO_{2+x}, $Cs_2U_2O_7$-UO_{2+x} and $Cs_2U_4O_{12}$-UO_{2+x} two-phase regions (Fig. 4).

IV. SUMMARY AND CONCLUSIONS

Cladding deformation adjacent to the interface of the uranium oxide blanket and the uranium-plutonium mixed-oxide fuel in fast-reactor fuel pins has been attributed to the formation of a low density Cs-U-O compound. Because of the large differences in molar volumes of the cesium uranates, the identity of the Cs-U-O compound is important in determining the volume increase. The Cs-U-O system was investigated in phase regions containing liquid cesium for which published data were conflicting. Thermodynamic data on the cesium uranates were estimated and used, along with data from the literature, to construct a cesium-uranium-oxygen phase diagram which is consistent with most of the experimental phase data. Thermodynamic and kinetic data have been used to show that, at the low oxygen potentials existing at the interface between the uranium oxide blanket and the uranium-plutonium mixed-oxide fuel, Cs_2UO_4 is the only Cs-U-O compound likely to be formed in the blanket.

ACKNOWLEDGMENTS

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61. The free energy values of $Cs_2U_6O_{19}$ and $Cs_2U_9O_{28}$ were chosen so that these compounds were unstable with respect to decomposition. Cordfunke *et al.*[17] and van Egmond[18,29-31] did not report a stable cesium uranate of the formula $Cs_2U_6O_{19}$. Cordfunke *et al.*[17] and van Egmond[18,29-31] assigned a chemical formula to an X-ray pattern after determining the unit cell from a Fourier analysis of the X-ray data. Efremova *et al.*[22] probably erred in assigning the formula $Cs_2U_6O_{19}$ to an X-ray pattern based on chemical analysis. This error is not surprising because of the small differences in chemical composition of the cesium uranates. Efremova *et al.*,[22] Cordfunke *et al.*[17] and van Egmond[18,29-31] agree that $Cs_2U_9O_{28}$ is not a stable cesium uranate.

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